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Supporting Information

Chemical Gardens as Electrochemical Systems: In Situ Characterization of Simulated Prebiotic Hydrothermal Vents by Impedance Spectroscopy

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Electrochemistry Calculations:

In order to make more sense of the measurement results, we need to review some concepts from electrochemistry. For the general redox reaction of the hydrothermal vent experiments

$$O + ne^- \rightarrow R \quad (1),$$

the thermodynamic equation that describes the reaction kinetics of free energy as a function of potentials E_{rxn} and reaction rate is

$$-\Delta G = nFE_{rxn} = RTlnK_{rxn} \quad (2).$$

where F is Faraday constant (96,485 C-mol^{-1}), R is the ideal gas constant, and T is the absolute temperature. The K_{rxn} is just the activity ratio of the reductant and oxidant described by the Nernst equation of the form

$$E_{rxn} = E_0 + \frac{RT}{nF} ln \frac{a_R}{a_O} \quad (3)$$

The redox potential (E_{rxn}) has contributions from both charge transfer (E_{ct}) and diffusion (E_{diff}) over-potentials

$$E_{rxn} = E_{ct} + E_{diff} \quad (4)$$

Both E_{rxn} and E_{diff} are electrochemically determined under equilibrium conditions by current approaching zero near the electrodes from impedances described by

$$\lim_{i \to 0} \frac{\partial E_{rxn}}{\partial i} = R_{ct} + R_{diff} \quad (5)$$

where the R_{ct} and R_{diff} are charge-transfer and diffusion resistances at rate limiting conditions with time; i.e., t → ∞.

Under our chimney experimental conditions (no forced convection), it can be correctly assumed that very minimal or no faradaic current crosses the electrodes, and mass-transfer controlled conditions from the concentration gradient within the diffusive-layer thickness (δ_{diff}) near the electrode interface as described by

$$\delta_{diff} = \sum_i \sqrt{\pi D_i t} \quad (6)$$

where D_i is the diffusion coefficient of species, i. The diffusion layer is described by Fick's 2nd law

$$\frac{\partial C_i}{\partial t} = -D_i \frac{\partial^2 C_i}{\partial x^2} \quad (7)$$

which relates the concentration gradient driving force of species i for redox to occur under sluggish kinetics with no forced convention (or unstirred) such as that of our simulated hydrothermal vent experiments. Figure S1 illustrates the behavior of diffusion controlled reaction kinetics adjacent the electrode interface using boundary conditions associated with non-steady-state conditions with the diffusion layer thickness growing with time.

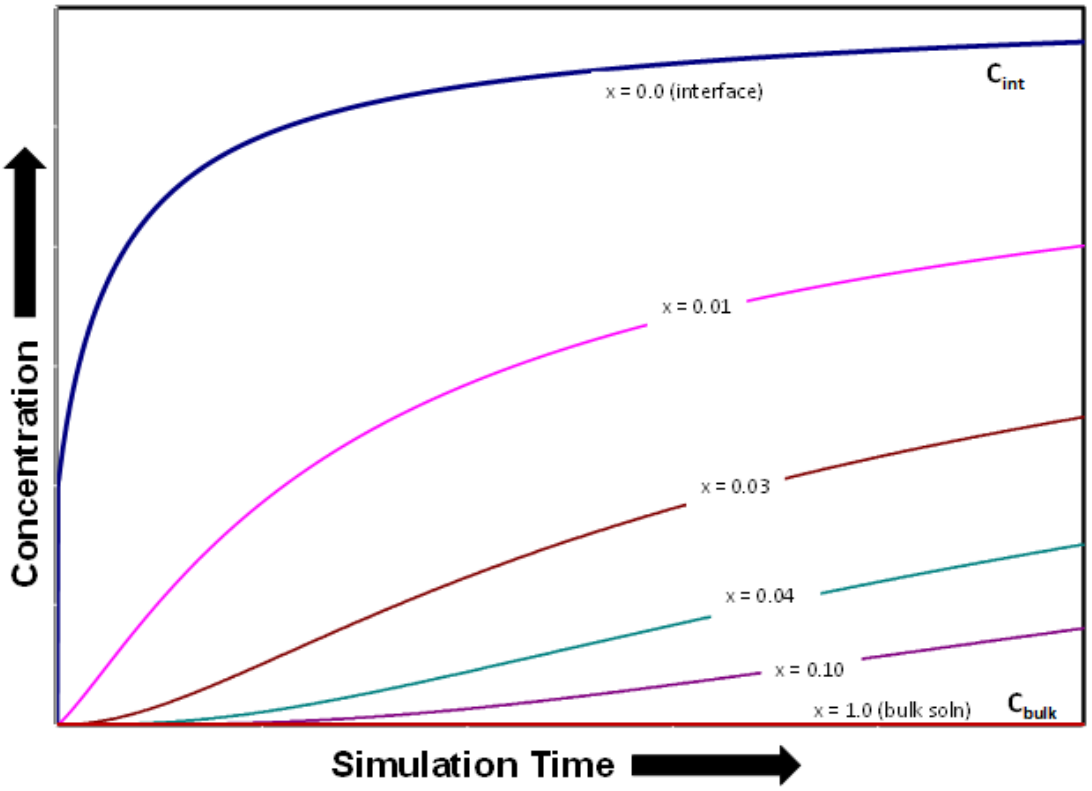

Figure S1: Numerical simulation of diffusion-controlled conditions on Fick's 2nd law. The concentration varies with laminae distance (x) from the electrode interface. Simulation was performed with boundary conditions $C(x=0, t=\infty) = C_{int}$, $C(x=\infty,t) = C_{bulk}$.

At the electrode interface, mass transport flux, J_{tot}, from all contribution of electroactive species *i* to its current density j_i occurs under both concentration and electric field gradients, which can be described by the Nernst-Planck equation

$$J_{tot}(x) = \sum_i \frac{j_i}{q_i} = \sum_i D_i \left[\frac{\partial C_i}{\partial x} + \frac{q_i F}{RT} C_i \frac{\partial \varphi(x)}{\partial x}\right] \quad (8)$$

where $\varphi(x)$ is the potential induced by charge carrier species *i* with charge magnitude q_i. Factoring in the charge mobility μ_i using the Einstein-relation, the current density j_{tot} equation is of the form

$$j_{tot} = \sum_i q_i u_i \left[\frac{\kappa_B T}{q_i} \frac{\partial n_i}{\partial x} + n_i \frac{\partial \varphi(x)}{\partial x}\right] \quad (9)$$

where n_i is the charge density of species *i*. Thereby, mass transport and electric field contributions at the electrode interface controls the electrochemistry as measured by current flow.

Electrochemical Impedance Spectroscopy:

Electrochemical impedance spectroscopy (EIS) can be a powerful technique in providing in-situ, non-destructive means for characterizing chemical dynamics of the simulated chimney experiment. Coupled with an electrode array, we were able to provide a direct means characterizing various local experimental environments real-time and continuously throughout the injection period of the experiment. The electrical properties are determined from the transform equation

$$Y^* = \frac{1}{Z^*} = \sigma^* Geo = j\omega\varepsilon_o\varepsilon^* Geo \quad (10)$$

where the symbol (*) represents all complex variables in admittance (*Y*), impedance (*Z*), conductivity (*σ*), and permittivity (*ε*). The *Geo* is defined as the geometric factor (area/length) of the electrode configuration.

In EIS, a small perturbation in potential (*η*) is applied so that an equilibrium condition is linearity maintained so the *i*-*η* relations results in

$$i_{tot} = \frac{-nFi_o}{RT}\eta = \frac{-\eta}{R_p} \quad (11)$$

where *R* is the gas constant, *T* is the temperature, n is moles e^- of the redox couple, F is faraday's constant, and i_o is the redox current. The polarization (R_p) impedance as measured by EIS is thus

$$R_p = \frac{-nFi_o}{RT} \quad (12)$$

For unstirred solutions containing electroactive species such as our simulated hydrothermal vent experiments, the R_p should be in the mass-transfer limited region driven by concentration gradient near the electrode interface as illustrated in Figure S1.

Reaction Rate Kinetics Characterization by EIS:

In addition to electrical properties, EIS is also capable of ascertaining reaction rate kinetics in the form of time constants. This is done using equivalent circuit modeling and extraction of circuit components values which are electrical representations of physical and chemical processes. In Figure 5 and 6, we highlighted some of the circuit model results from EIS measurements on all three local environments on the control fuel cell experiments and on the actual simulated chimney experiment. For mass-transfer limited kinetics using the electrode array, a circuit with one or two relaxation (RC-unit) time constants in series with a resistor (uncompensated solution resistance) is used to describe the frequency dispersions of measured spectra. The single time constant provides the best fit for EIS measurements over multi-phase materials while two time constants is best for single phase materials due to the significant gradients of materials interactions at the two electrodes. Ostensibly, diffusion limit occurs at the lowest frequencies and it is useful to describe this phenomenon using a pseudo-capacitive circuit component known as the constant phase element (Z_{CPE}) due to the non-uniformity of the electrode surface. The general formula describing the equivalent circuit with two time constants is

$$Z(\omega) = R_0 + \frac{R_1}{j\omega\tau_1+1}\,\frac{R_2+Z_{CPE}}{j\omega(\tau_2+C_2Z_{CPE})+1} \quad (13)$$

where the time constants $\tau_1 = R_1C_1$ and $\tau_2 = R_2C_2$.

For mass-transfer controlled kinetics, the relaxation time constant(s) are mostly attributable to double-layer charging at the two electrode interfaces. The fuel cell control experiments exhibited increases in both the double-layer capacitances and ionic resistances in the ocean and hydrothermal fluid baths (see Figure 3). However, across the membrane substantial decreases in capacitances and resistances were observed indicating formation of more electroactive species as driven by concentration gradients between the membranes. Similarly in the chimney experiments, the electroactive species is the buildup of hydrothermal precipitates as measured within the chimney. Across the chimney interface and ocean bath, the capacitance and resistance were substantially higher indicating materials gradients between the ocean and the chimney providing the driving force necessary for chimney formation. In Table 1, we summarized the time constants for double-layer kinetics. In the membrane and within the chimney, the time constants were determined at $9.4\text{x}10^{-1}$ sec and $1.0\text{x}10^{-2}$ sec, respectively, which are substantially higher than ocean baths and further substantiates the presence of the more electroactive species throughout each experiment.

Table 1. Comparison of double-layer time constants on control and simulated hydrothermal chimney experiments from circuit modeling.

	Fuel Cell Control Exp.			Sim. Hydrothermal Chimney Exp.		
	Membrane	HV bath	Ocean bath	Inside	Interface	Ocean
R_0 (Ω/cm^2)	55.4	124.7	59.6	4.1	32260.0	38850.0
C_1 ($\mu F/cm^2$)	109.7	76.0	18.2	2440.0	1.2	1.2
τ_1 (sec)	9.4E-01	9.5E-03	1.1E-03	1.0E-02	3.8E-02	4.6E-02

As EIS is essentially an alternating current (ac) measurement, we also extracted the capacitances at the diffusion-limited frequencies as it relates to free energy measurements within the hydrothermal precipitates throughout the experiment. Recall, the relationship

$$q = CV \quad (14)$$

which relates the charge (q), capacitance (C), and applied potential (V). The limiting diffusion current (i_{diff} = dq/dt) is therefore is described by the equation

$$i_{diff} = C\frac{dV}{dt} \quad (15)$$

as a function of capacitance, potential, and time. With the electrode array, we were also able to probe various local potentials throughout the experiment along with measurement of the impedance.